



## Fullerene-mediated electro-synthesis of Ag–C<sub>60</sub> nanocomposite in a water-organic two-phase system

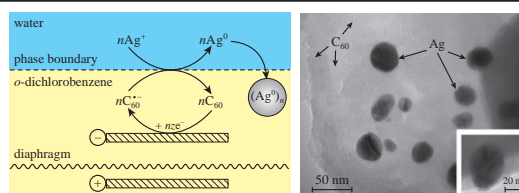
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**By example of fullerene-mediated electro-synthesis of Ag–C<sub>60</sub> nanocomposite in water–*o*-dichlorobenzene, the possibility of using a liquid–liquid two-phase system for the electro-synthesis of metal nanoparticles has been demonstrated for the first time.**



The chemical reduction of metal ions (complexes) in water-organic two-phase systems known as the Brust–Schiffrin method<sup>1,2</sup> is among the efficient methods for synthesizing ultra-small monodispersed metal nanoparticles (M-NPs). Faraday<sup>3</sup> was the first to use a two-phase system to obtain Au-NP (colloidal gold) by reduction of a gold salt in aqueous solution with elementary phosphorus in carbon disulfide. A distinctive feature of the method is that both the reducing agent and the metal ion are initially located in different liquid phases, while the M-NPs are stabilized in one of the phases. This method was used to obtain ultra-small NPs of gold,<sup>1,4–7</sup> silver,<sup>5,7–10</sup> palladium<sup>10,11</sup> and copper.<sup>5,7,12–14</sup>

The electrochemical methods for synthesizing M-NPs in the solution bulk are commonly based on the reduction of metal ions directly on the electrode, e.g. the pulse sonochemistry method<sup>15–17</sup> and the Reetz method.<sup>18–22</sup> However, these methods do not allow one to employ this efficient approach in a two-phase system in full measure, since, by definition, cathode and metal ion should be located in two different phases. On the other hand, the use of two-phase system may be quite helpful in mediated electro-synthesis of M-NPs<sup>23–33</sup> for both synthesizing ultra-small NPs and expanding the method capabilities, in particular, improving the process efficiency.

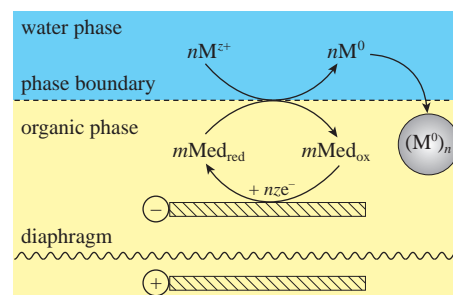
A two-phase system would make it possible to use metal salts (complexes) soluble in water (organic phase) but insoluble in an organic phase (water), and mediator compounds soluble in an organic phase (water) but insoluble in water (organic phase), within the same experiment. This feature prevents the reduction of the metal ions directly on the electrode and metal deposition on it, which is the main problem that limits the electrochemical reduction of metal ions during the preparation of M-NPs in the solution bulk. M-NP electro-synthesis with large ratios between metal ion and mediator can be accomplished in two-phase system, even if the metal salt is partially soluble in the organic phase and the metal ion is reduced directly on the electrode more easily than the mediator. Furthermore, the oxidation of the M-NPs generated on the anode, which is possible in the course of the electrolysis in an undivided cell, is totally prevented.

Hypothetically, it seems that a few versions of mediated electro-synthesis in a two-phase system can be implemented. This

communication presents the first example of the M-NP electro-synthesis version in a water-organic two-phase system (Figure 1), viz., the C<sub>60</sub> fullerene mediated electro-synthesis of Ag-NPs in a water–*o*-dichlorobenzene (DCB) performed in a divided cell.

In this case, the fullerene is attractive as a mediator for the following reasons: (i) it is soluble in DCB and insoluble in water;<sup>34</sup> (ii) it can reversibly accept up to six electrons per molecule in a stepwise manner,<sup>35–37</sup> and hence it can act as a mediator transferring one or more electrons from the electrode to the substrate;<sup>38–43</sup> (iii) radical anions and dianions are not protonated by such proton donors as water or phenol,<sup>44–47</sup> i.e. these species would not be consumed in side reactions in contact with aqueous phase under the conditions of their generation; (iv) by analogy with the C<sub>60</sub>-mediated electro-synthesis of the Au–C<sub>60</sub> nanocomposite in DCB–DMF medium,<sup>31</sup> one may believe that the fullerene would serve as not only a mediator at potentials of the C<sub>60</sub>/C<sub>60</sub><sup>•-</sup> redox couple, but also as a stabilizer of the generated Ag-NPs, eventually giving the Ag–C<sub>60</sub> nanocomposite. Such silver-based nanomaterials are very promising for applications in biology and, particularly, for surface-enhanced Raman spectroscopy in medical diagnostics.<sup>48,49</sup>

Initially, the organic phase (12 ml), hosting a glass-carbon cathode ( $S = 5.6 \text{ cm}^2$ ), contains the fullerene (2.0 mM) and Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) as the supporting electrolyte, while the aqueous phase (4 ml) contains AgNO<sub>3</sub> (1.5 mM) and NaBF<sub>4</sub> (0.1 M). Upon stirring the solution, the fullerene is not transferred to the



**Figure 1** The mediated electro-synthesis of M-NPs in a water-organic two-phase system performed in a divided cell.